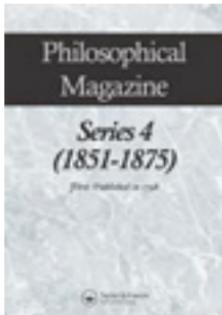


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XII. On a new chemical theory

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XII. *On a New Chemical Theory.*
By ARCHIBALD S. COUPER, Esq.*

THE end of chemistry *is its theory*. The guide in chemical research *is a theory*. It is therefore of the greatest importance to ascertain whether the theories at present adopted by chemists are adequate to the explanation of chemical phenomena, or are, at least, based upon the true principles which ought to regulate scientific research.

Among those which have lately been developed, there is one, on account of its apparently numerous merits, which particularly claims investigation, and respecting which we deem that it would not be unprofitable were either new proofs of its scientific value furnished, or, on the contrary, should considerations be adduced establishing not only its inadequacy to the explanation, but its ultimate detriment to the progress of science. I allude to the system of types as advocated by Gerhardt.

This system, striking alike for the breadth of its conception, and the logical and consequent manner in which it has been developed, has been controvèrted from the point of view afforded by theories less far-reaching than the one under consideration, and even based upon a one-sided and restricted appreciation of certain chemical reactions. The consequence is that this opposition has not impaired the favour with which the unitary system has been received, but has rather tended to display it in a more advantageous light.

Imposing as this theory is, it is nevertheless all the more necessary to submit it to a strict investigation; for there is nothing so prejudicial in the search for truth as the blind spirit of conservatism. A rational belief demands the test of a preliminary doubt.

There are two conditions which every sound theory must fulfil:—

1. It must be proved to be empirically true.
2. It must no less be philosophically true.

I admit that this theory is for the most part empirically true, that is to say, it is not contradicted by many of the facts of the science. Evidence that this condition is only partially fulfilled, is to be found—

1. In the circumstance that the peroxides, for instance, do not fit very satisfactorily into the types.
2. The principle of double decomposition cannot well be applied to the conversion of the anhydrous sulphuric acid into the hydrate of that acid by the action of one equivalent of water,

* Communicated by the Author.

the formulae of these bodies being, according to Gerhardt, in their free state $O.SO^2$ and H^2O . Combined, they become simply SH^2O^4 .

The same remark applies in like manner to carbonic acid. In these instances the wonted consequence of Gerhardt is missed. The fact of the density of the vapour of these bodies being the same in the free as in the combined states, may have prevented him from doubling the formulae of these anhydrous acids. The types of this theory being *essentially types* of double *decomposition*, this instance of simple combination diminishes somewhat the value of the otherwise great logical merit of this system.

Having taken notice of such exceptions, the empirical truth of the theory may be otherwise admitted.

The philosophical test demands that a theory be competent to explain the greatest number of facts in the simplest possible manner.

In applying this test, three aspects of it require to be taken into consideration :—

1. As to the extension of the theory.
2. The explanation it affords of the facts.
3. The manner of this explanation.

As to the first: this theory indeed brings every chemical combine under a certain comparative point of view with every other. Herein apparently is its merit. Nevertheless, should our test be applied to its full extent, it will be found that it is fatal to this system, in other respects so imposing. The comparative point of view which it adopts is fundamentally false.

As to the second : it does not explain the facts at all ; consequently the most essential point of the test is unfulfilled.

3. This condition of the test is in like manner unfulfilled, from the fact of the second not being complied with.

Why is it that Gerhardt's theory so signally fails in these two essential requisites? Because it is based upon an old but vicious principle, which has already retarded science for centuries. It begins with a generalization, and from this generalization deduces all the particular instances. But it does not come within the limits of a chemical paper to enter upon a discussion which is purely metaphysical. Nevertheless the theory of Gerhardt can only be combated upon metaphysical grounds, because it is only in overturning a general principle of research that the theory can be proposed. Gerhardt's generalization lacks, moreover, the merit of being represented by a type having a known existence.

$nO^H_{H^2}$, from which he derives every chemical combine, being in itself indefinite, cannot of course be contained or be produced in any definite body. That, however, which may be demanded

of the type is, that in itself it should afford at least an instance of that which it is meant to represent. Now the part "n" of the type represents the notion of indefinite multiples of $O\frac{H}{H}$. But not a single instance of a multiple of $O\frac{H}{H}$ has been proved to exist;

much less has it been proved that there exists, or can exist, multiples of this body in an indefinite series. The perfection or imperfection of the type meant to represent the generalized notion, is, however, a matter of comparatively inferior moment. It is the principle involved in this generalization which is essentially pernicious.

Should the principle which is therein adopted be applied to the common events of life, it will be found that it is simply absurd. Suppose that some one were to systematize the formation of letters into words that formed the contents of a book. Were he to begin by saying that he had discovered a *certain word which would serve as a type, and from which by substitution and double decomposition all the others are to be derived*,—that he by this means not only could form new words, but new books, and books almost *ad infinitum*,—that this word also formed an admirable point of comparison with all the others,—that in all this there were only a few difficulties, but that these might be ingeniously overcome,—he would state certainly an empirical truth. At the same time, however, his method would, judged by the light of common sense, be an absurdity. But a principle which common sense brands with absurdity, is philosophically false and a scientific blunder.

Suppose the book that had formed the basis of this system were a German one, where all the words were found to be composed at least of two letters, still even in this language the viewing and systematizing of words as a series of double decompositions would be no less ridiculous.

The sure and invincible method of arriving at every truth which the mind is capable of discovering is always one and the same. It is that, namely, of throwing away all generalization, of going back to first principles, and of letting the mind be guided by these alone. It is the same in common matters. It is the same in science. To reach the structure of words we must go back, seek out the undecomposable elements, viz. the letters, and study carefully their powers and bearing. Having ascertained these, the composition and structure of every possible word is revealed. It would be well to call to recollection the parallelism of chemical research with that of every other search after truth; for it has been in overlooking this that in chemistry false and vacillating theories have been advocated and a wrong route so

often pursued. In mathematics the starting-point is not generalizations, but axioms, ultimate principles. In metaphysics Descartes led the way of progress by analysing till he thought he could reach some ultimate elements beyond which it was impossible for him to go, then studying their force and power, and proceeding synthetically. The recognition of this method wrought the regeneration of science and philosophy.

On the other hand, look where Gerhardt's generalization of Williamson's generalization leads him, and legitimately too,—a fact which his logical spirit clearly discerned. He is led not to explain bodies according to their composition and inherent properties, but to think it necessary to restrict chemical science to the arrangement of bodies according to their decomposition, and to deny the possibility of our comprehending their molecular constitution. Can such a view tend to the advancement of science? Would it not be only rational, in accepting this *veto*, to renounce chemical research altogether?

These reflections naturally lead to the inquiry after another theory more adequate to satisfy the just demands which can be made upon it. There is one which, as it is still supported by many distinguished chemists, cannot be passed over altogether unnoticed. It is that of the theory of certain combinates in organic chemistry which are to be viewed as analogous to, "playing the part of," inorganic elements. These are denominated radicals, and are supposed to be contained in all organic chemical products.

In addition to this, and also in connexion with it, there is a doctrine describing many combinates to be copulated, conjugated, by addition.

It is impossible here to enter upon any extensive criticism of this theory. I can only remark that it is not merely an unprofitable figure of language, but is injurious to science, inasmuch as it tends to arrest scientific inquiry by adopting the notion that these quasi elements contain some unknown and ultimate power which it is impossible to explain. It stifles inquiry at the very point where an explanation is demanded, by putting the seal of elements, of ultimate powers, on bodies which are known to be anything but this.

Science demands the strict adherence to a principle in direct contradiction to this view. That first principle, without which research cannot advance a step, dare not be ignored; namely, that a whole is simply a derivative of its parts. As a consequence of this, it follows that it is absolutely necessary to scientific unity and research to consider these bodies as entirely derivative, and as containing no secret ultimate power whatever, and that the properties which these so-called quasi elements possess are a

direct consequence of the properties of the individual elements of which they are made up.

Nor is the doctrine of bodies being "conjugated by addition" a whit in advance of that which I have just been considering. This doctrine adopts the simple expedient of dividing certain combinates, if possible, into two imaginary parts, of which one or both are bodies already known. Then it tells us that these two parts are found united in this body. But how they are united, or what force binds them together, it does not inquire. Is this explication arbitrary? Is it instructive? Is it science?

I may now be permitted to submit a few considerations relative to a more rational theory of chemical combination.

As everything depends upon the method of research employed, it will in the first place be necessary to find one that may be relied upon. If the method is good and conscientiously carried out, stable and satisfactory results may be expected. If, on the contrary, it is vicious, we can only expect a corresponding issue. A satisfactory method is, however, not difficult to find, nor is it difficult in its application.

The principle which ought to guide all research is in every case the same. It is that of analysing till it is impossible to reach more simple elements, and of studying these elements in all their properties and powers. When all the properties and powers of the individual elements are known, then it will be possible to know the constitution of the combinates which their synthesis produces. It is necessary therefore in chemical research, in order to ascertain the various qualities and functions of the different elements,—

1. To consider the whole of chemistry as one.
2. To take into consideration every known combinata, and to study the character, functions, and properties displayed by each element for itself, in each of these combinates in all their different conditions and aspects. It is by a comparison of the different bodies among themselves that we are able to trace the part that is performed by each element separately.
3. To trace the general principles common to all the elements, noting the special properties of each.

This method is essentially different from that where one class of bodies is chosen as a point for the restriction of our views of the properties of the others—where only the qualities found in the first are to be measured out to the rest.

I shall now proceed to inquire how its more thorough application tends to the development of a rational chemical theory.

It has been found that there is one leading feature, one in-

herent property, common to all the elements. It has been denominated chemical affinity. It is discovered under two aspects :—
(1) affinity of kind ; (2) affinity of degree.

Affinity of kind is the special affinities manifested among the elements, the one for the other, &c., as carbon for oxygen, for chlorine, for hydrogen, &c.

Affinity of degree is the grades, or also limits of combination, which the elements display. For instance, C^2O^2 and C^2O^4 are the degrees of affinity of carbon for oxygen. C^2O^2 may be called the first degree, and C^2O^4 may be termed the second degree, and, as a higher degree than this is not known for carbon, its ultimate affinity or combining limit. Affinity of degree in an element may have only one grade. It may have, however, and generally has more than one. Here then is an inherent property common to all elements, by the removal of which the chemical character of an element will be destroyed, and by virtue of which an element finds its place marked out in a complex body.

It is such a property that is required to form the base of a system. Nor would its suitableness for this purpose be affected by the discovery that the elements are themselves composite bodies, which view the chemist is perhaps not unwarranted to adopt. For in such a case the necessity would doubtless still be found to exist of adopting the principle of affinity, or something at least equivalent to it, as the basis of the explanation of chemical combinates. In applying this method, I propose at present to consider the single element carbon. This body is found to have two highly distinguishing characteristics :—

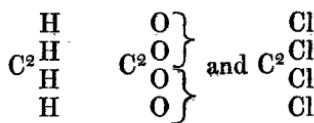
1. It combines with equal numbers of hydrogen, chlorine, oxygen, sulphur, &c.

2. It enters into chemical union with itself.

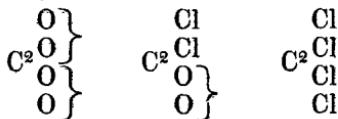
These two properties, in my opinion, explain all that is characteristic of organic chemistry. This will be rendered apparent as I advance.

This second property is, so far as I am aware, here signalized for the first time. Evidence as to its being a property of carbon may therefore be required.

It will be found in the following :—What is the link which binds together bodies composed of 4, 6, 8, 10, 12, &c. equivalents of carbon, and as many equivalents of hydrogen, oxygen, &c.? In these you may remove perhaps all the hydrogen or oxygen, and substitute so many equivalents of chlorine, &c. It is then the carbon that is united to carbon. Further, that it is not the hydrogen that is the binding element in these combinates is evident ; thus—

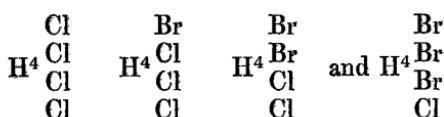


Here the whole four of hydrogen are not bound by a mutual affinity; for each element of hydrogen can be substituted for one of chlorine in regular series, beginning with the first and ending with the last. The atoms of oxygen are, on the contrary, united in pairs (which will be more fully developed hereafter), and only for two atoms of oxygen two of chlorine can be substituted; thus—



In the same manner with bodies that contain multiples of C² united to hydrogen, &c.

Take the inverse of this. If the four atoms of hydrogen were bound together, we could evidently expect to form such bodies as



or for bodies like $C^4 H^4$, $C^6 H^6$, $C^8 H^8$, one would naturally expect to find the carbon substituted for chlorine, and find bodies like $H^4 Cl^2$, $H^6 Cl^6$, $H^8 Cl^8$ &c.

These bodies are not only unknown, but the whole history of hydrogen might be investigated and not a single instance be found to favour the opinion that it has any affinity for itself when in union with another element.

Now, on the other hand, carbon remains chemically united to carbon, while perhaps 8 equivalents of hydrogen are exchanged for 8 equivalents of chlorine, as in naphthaline. Analogous to this is the conversion of alcohol, $C^4\frac{O}{H^5}OH$, and the hydrocarbon C^4H^6 into C^4Cl^6 . All the countless instances of substitution of chlorine, &c. tend in the same direction. They prove beyond doubt that carbon enters into chemical union with carbon, and that in the most stable manner. This affinity, one of the strongest that carbon displays, is perhaps only inferior to that which it possesses for oxygen.

Another feature in the affinity of carbon is, that it combines by degrees of two; thus, C_2O_2 and C_2O_4 , C_4H_4 and C_4H_6 .

C^6H^6 and C^6H^8 , C^8H^8 and C^8H^{10} , &c.: from these last it is especially evident that two is the combining grade of carbon. It becomes still more apparent when we compare the bodies

C^4H^4 and C^4H^5Cl , that is, $C^4H\left.\right\{Cl\atop H^4}\&c.$. Many such proofs might

be added, while on the other hand there are no instances contradictory of this point. Hence the circumstance that it must ever remain impossible to isolate a combine of the form C^2H^3 or C^4H^5 , &c.

Carbon having only two grades of combination of two atoms each, a fact which is easily traced throughout all organic chemistry, this inherent property of the element may legitimately furnish two grand types for all its combinates.

The first type will be nC^2M^4 .

The second type will be $nC^2M^4 - mM$.

As examples belonging to the first type, may be mentioned the alcohols of the æthylic form, their ethers, the fatty acids, &c.

Thus methylic alcohol has the formula $C^2\left.\right\{O\atop H^3}OH$, and æthylic

alcohol, $C^2\left.\right\{O\atop H^2}H^3$.

In these instances it will be observed, that for each double atom of carbon the combining power is (4) four, which is the ultimate limit of combination for carbon in all bodies yet produced.

In the latter instance it is apparent, inasmuch as if the combining limit of two C^2 's be each reduced by 3 in hydrogen or oxygen, there still remains a combining power of *one* to each of the two C^2 's which each expends in uniting with the other;

therefore C^2H^3 , or what is the same thing, $C^2\left.\right\{H^2\atop C^2H^3}$ belongs to the type nC^2M^4 .

Again, the inherent properties of the elements may be viewed as dividing bodies into primary, secondary, tertiary, and so on combinates. These may be termed so many orders of complicity. Thus C^4H^6 is a primary combinata, or it belongs to the first order of complicity; but $C^4\left.\right\{O\atop H^5}OH$ is a secondary combinata, or belongs to the second order of complicity. C^2O^2 and C^2O^4 are primary, while C^2O^4 , $2OH$ and C^2O^4 , $2OKa$ are secondary.

A primary combinata is then nC^2 united to nM^4 or to $nM^4 - mM^2$

in such a manner that the combining energy of the complement (nM^4 , &c.) either *potentially or actually* does not extend beyond nC^2 .

A secondary combine is one in which the combining energy of the complement is not all expended upon nC^2 , but is extended further to one or more elements.

On the same principle there are tertiary combines, &c.

These orders of complicity ought in reality to be subdivided. This, however, I do not think it necessary for the present to enter upon. It will now be understood why an alcohol belongs to the type $nC^2 M^4$, and on the same principle why a free aether

belongs to the same type, thus $\begin{array}{c} C^2 \cdots O \cdots \\ \vdots \cdots H^2 H^2 \cdots \\ C^2 \end{array}$, while they are $C^2 \cdots H^3 H^3 \cdots C^2$

at the same time secondary combines.

A secondary combine, that is to say, a body belonging to the second order of complicity, is, as will be understood from the principle which forms the ground of the rational theory, a direct consequence of an inherent property of one or more of the elements which form the complement to the carbon.

In the instance before us, it is a certain property of the oxygen which is the cause of the secondary combine. This property is the affinity which one atom of oxygen in combination always exerts towards another atom of oxygen likewise in combination.

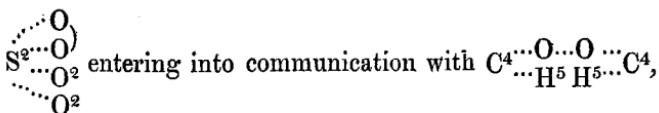
This affinity is modified by the electric position of the element to which the respective atoms of oxygen are bound. From this property results the fact, that in organic combines the atoms of oxygen are always found double.

For instance, the combining limit of oxygen being two, when two molecules of $\begin{array}{c} C^2 \cdots O \cdots \\ \vdots \cdots H^2 \cdots \\ C^2 \cdots H^3 \end{array}$ are set at liberty, the free affinities of

the oxygen instantly produce the union of these molecules. The cause of the union of two molecules of $C^2 H^3$ has been already remarked. In the two cases, the causes of the union of the respective molecules are in so far different, that the one is the result of a property of the carbon, while the other is the result of a property of the oxygen.

The view here adopted of the nature of oxygen is, I am convinced, alone in conformity with the reactions where the properties of this body develop themselves.

The vapour of anhydrous sulphuric acid, for instance, is conducted into anhydrous aether. The following will then be the reaction:—



the two atoms of the oxygen of the sulphuric acid and the two atoms of the oxygen of the æther (now in presence of each other) being in different (perhaps different electric) conditions, mutually loosen their former affinities and reunite themselves to the (electrically ?) different atoms of oxygen of these respective combinates.

The same principle may naturally be expected to display itself with regard to acids and bases. The oxygen of an acid unites itself to the (electrically ?) different oxygen of water. The oxygen of a base on the same principle has an affinity for the electrically different oxygen of water.

It will be observed—

1. That the oxygen of the water of an acid can only be expelled by that of a base, and *vice versa*.

2. It is to be remarked that *it is not* the metal of a base which exchanges places with the hydrogen of the hydrate of an acid; for if that were the case, the affinity of the oxygen of the metal, and also of the acid, *would be greater for the oxygen of the water than the affinity of the hydrogen for that same oxygen*. But this is not so. The very opposite is the truth. If one atom of hydrogen be withdrawn from the hydrate of an acid or from *the hydrate of an oxide*, *it is universally accompanied by an atom of oxygen*. It is evident, then, that the affinity between *the positive and negative atoms of oxygen is less than that which attaches these atoms to the element with which they form a primary combine*.

A consequence of this truth is, that it is impossible to double the equivalent of oxygen, if the chemical equivalents are to be understood as not being in direct contradiction to any chemical truth or essential feature in the properties of an element. Carbon differs entirely in this respect from oxygen.

There is no reaction found where it is known that C^2 is divided into two parts. It is only consequent therefore to write, with Gerhardt, C^2 simply as C, it being then understood that the equivalent of carbon is (12) twelve.

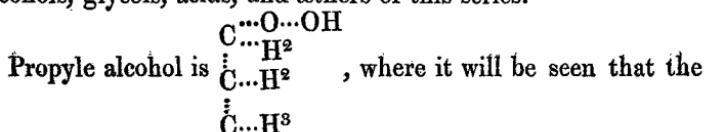
This value of the atom will be adopted in the following part of this paper.

Sulphur, selenium, &c. being bodies displaying properties similar, not to carbon, but to oxygen, it will be necessary to retain the equivalent value that has generally been assigned to them.

I have now shown how ordinary alcohol, $\text{C}^2 \text{H}^6 \text{O}^2$, common æther, and the hydrocarbide, $\text{C}^2 \text{H}^6$, belong to the type $n\text{CM}^4$.

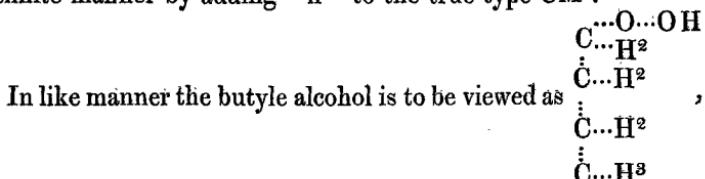
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The phenomena which necessitate this view of the constitution of these bodies have a like consequence in regard to the other alcohols, glycols, acids, and æthers of this series.

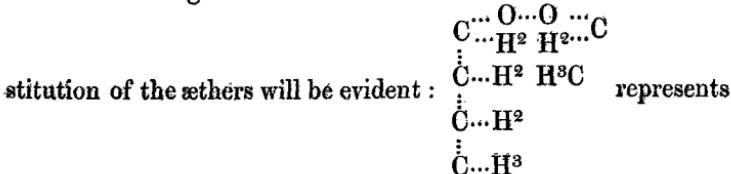


atom of carbon situated between the two others, on account of being chemically united to these, is reduced to the combining power of two for hydrogen, oxygen, &c. One combining power is given up to the carbon upon the one side, and a second to the carbon upon the other.

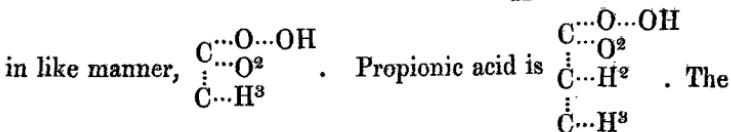
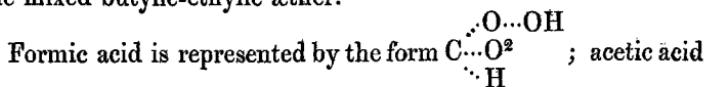
It will be observed also, that the primary combinates ought in rigour to be themselves enumerated in an inverse order. The type $n\text{CM}^4$ becomes then in reality the type CM^4 . This enumeration, however, does not appear to possess any great practical utility, and it is perhaps preferable simply to denote it in an indefinite manner by adding "n" to the true type CM^4 .



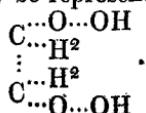
and so on throughout all the series of these aleohols. The con-



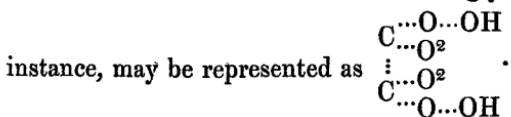
the mixed butylic-ethylic æther.



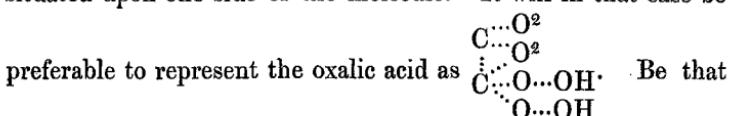
constitution of glycol may be represented as follows :—



In like manner as to the acids of these glycols; oxalic acid, for



Respecting these acids, it may perhaps be allowable to suggest the possibility of the molecule having two poles, and that especially the atom of oxygen situated at one or perhaps both, and near to two atoms of oxygen bound together, and forming no secondary combinative, may be in a state presenting great affinity for basic oxygen. Analogy with the electric poles may perhaps demand the opinion that all the negative oxygen be situated upon one side of the molecule. It will in that case be



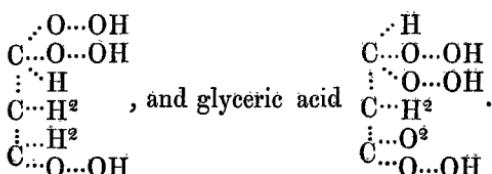
as it may, however, the rational method of investigation proves it to be a law, that in acids of the type $n\text{CM}^4$ the presence of two atoms of oxygen bound together so as to form only a primary part of the same molecule, and situated close to the negative oxygen, is necessary to the calling forth or production of this negative state.

This is a particular instance, but it moreover shows generally how the electro-positive or the electro-negative value of the elements mutually modify and condition the electro-positive or electro-negative value of each other when in combination.

This law is different from the electric hypothesis which chemists have formerly defended, but which never could be traced throughout a thoroughgoing application of their views to organic chemistry.

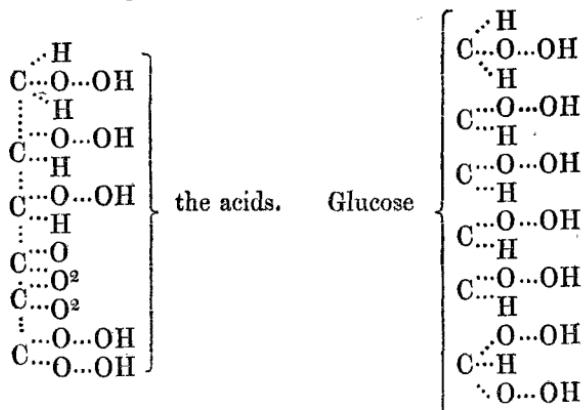
The law here distinctly enounced coincides exactly with, and is rendered apparent by the application of the theory of chemical combination which I support.

But to return. Glycerine is



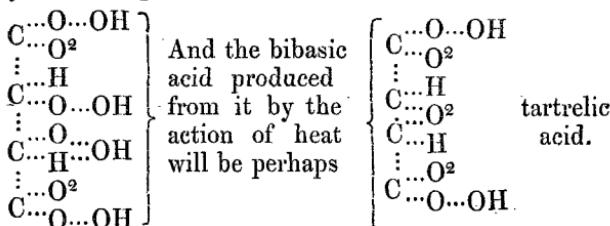
Glucose has been perhaps too little investigated to afford data sufficient to determine definitely its formula. Taking, however, mucic and saccharic acids as starting-points, these bodies may

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be meanwhile represented as—



It will thus be seen that these combinates all belong to the type NCM^4 .

Many others might be added. For instance, tartaric acid:—



It is my intention to consider, in a future communication, the second type, and to apply my views to the cyanogen combinates, &c.

XIII. Note on the Algebraical Theory of Derivative Points of Curves of the Third Degree. By J. J. SYLVESTER, Professor of Mathematics in the Royal Military Academy*.

TWO years and upwards have elapsed since I discovered the extraordinary theorem in the doctrine of cubic forms which I am about to state, but which has never yet been published by me, although communicated in confidence to a few friends, including Mr. Cayley. It arose out of purely arithmetical speculations relating to such forms, to some of which I may make a brief allusion in the course of this note.

If we suppose the general homogeneous equation of the third

* Communicated by the Author.